Thermodynamically Consistent Method of Determination of the Critical Parameters for Reference Data Tables

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Optimal choice of the critical parameters determines to a great extent the quality of proposed equations of state for calculating thermophysical properties in a wide neighborhood of the critical point. In this report the authors propose a simple method of determining "optimal" as to quality of description of thermal properties on the binodal values P_C, T_C and $\tilde{\rho}_C$. Ozone–safe refrigerants R32, R125, R134a, R143a and R152a were considered as objects of this study. Determination of the critical parameters was made by several steps. The first of them was statistical analysis of the know literature data on the critical parameters of the studied objects: abnormality of separate values of existing sampling was evaluated, and mean-weighted values of P_C, T_C and ρ_C were calculated together with their confidence intervals. The second step was an approximation of literature data on thermal properties of substances on the saturation line with the following system of equations:

$$\ln \omega' = B_1 \tau'^{F_1(\cdot)},\ \ln \omega'' = B_2 \tau''^{F_2(\cdot)},\ \Delta\rho = \rho' - \rho'' = B_0 t^{F(\cdot)},\ \ln \pi = \alpha_R \tau + b\tau^c \qquad (1)$$

where $\omega' = \rho'/\tilde{\rho}_C$, $\omega'' = \rho''/\tilde{\rho}_C$, $\pi = P/\tilde{P}_C$ denote reduced values of density and pressure; B_1, B_2, B_0 denote amplitudes depended on individual properties of substances; α_R denotes the Riedel's criterion; $\tau = \ln(\tilde{T}_C/T)$, $t = 1 - T/\tilde{T}_C$ denote reduce temperatures; F_1, F_2, F denote crossover functions, universal for non-associated substances, and β_1, β_2, and β - denote critical indices. A characteristic feature of the proposed equations (1) is the independence of the coefficient values B_1, B_2, B_0, β_1, β_2, β, α_R, b, c from the volume of the initial information. Minimal values of mean-square deviations of initial data on density and pressure of saturated vapor from the ones calculated with equations (1) were criteria for optimal choice of the parameters, the values of P_C, T_C and $\bar{\rho}_C$ being varied in the confidence interval boundaries. The degree of thermodynamic accordance of the critical parameters and thermal properties on the binodal can be evaluated for the amplitudes B_2, B_1, B_2, together with the character of variation of d^2T/dT^2 in the vicinity of the critical point.